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Measuring Intermolecular Excited State Geometry for Favorable Singlet Fission in Tetracene

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Abstract

Singlet fission (SF) is the process of converting an excited singlet into a pair of excited triplets. Harvesting two charges from a single photon has the potential to increase photovoltaic device efficiencies. Acenes, such as tetracene and pentacene, are model molecules for studying SF. Despite SF being an endoergic process for tetracene and exoergic for pentacene, both acenes exhibit near unity SF quantum efficiencies, raising questions about how tetracene is able to overcome the energy barrier. Here, we use recently developed instrumentation to measure inelastic neutron scattering (INS) while optically exciting the model molecules using two different excitation energies. The spectroscopic results reveal the structural changes due to the formation of a triplet

excimer complex. The excimer and the structural dynamics of the surrounding tetracene molecules are studied using time-dependent density functional theory (TD-DFT), which shows that the singlet and triplet levels shift due to the excited state geometry, removing the uphill energy barrier for SF.

Introduction

Photovoltaics (PV) convert sunlight into electricity with zero emissions, providing technical solutions for both the worlds ever-growing energy demand while simultaneously preventing climate change from CO₂ emissions. The Shockley-Queisser limit¹ defines the maximum theoretical single junction PV device efficiency at $\sim 33\%$. Singlet fission (SF) is a spin allowed process that converts a singlet exciton into a pair of triplet excitons between molecular chromophores. This carrier multiplication process increases the maximum theoretical PV efficiency to $\sim 44\%$.^{2,3} Converting a single photon into a pair of excited charges spurred research into the use of SF molecules to improve PV device efficiency, as the ability to overcome the Shockley-Queisser limit would have profound impacts on the price and land use of PV. While SF is not fully understood, many studies have been dedicated to molecules that can undergo SF and into incorporating SF into devices for increased efficiencies,⁴⁻⁷ including photovoltaics,⁸⁻¹⁶ photodetectors,¹⁷ and organic light emitting diodes.¹⁸⁻²¹

A simplified general mechanism for SF is:



where S_0 and S_1 are the singlet ground and first excited states, respectively, $(TT)^1$ is the correlated triplet pair state, and T_1 is the first excited triplet state. SF is a unidirectional process when $E(2T_1) \leq E(S_1)$ and reversible when $E(2T_1) \geq E(S_1)$.²² It is well-known and widely accepted that $E(S_1) \geq E(2T_1)$ or $E(S_1) \approx E(2T_1)$ leads to efficient formation of T_1 states via SF. However, if $E(S_1) < E(2T_1)$, then even if $(TT)^1$ forms, it should relax back to S_1 . SF in

tetracene has been examined in some detail because it appears to break this energetic argument. Excited state energy measurements in tetracene clearly indicate that $E(S_1) < E(2T_1)$ but excitation of tetracene to S_1 still results in formation of T_1 . The source of energy and the mechanism to overcome the energy barrier in the cases of $E(S_1) < E(2T_1)$ remains inconclusive. Experimental and theoretical studies suggest that the energy deficit can either be obtained through a thermally activated process,²³ with singlet fission from higher lying singlet states (S_n),²⁴ compensated entropically,²⁵ or through the formation of multiexciton states.²⁶ However, these theories contradict the independence of SF to excitation energy^{27,28} and temperature.²⁹

Here, we use inelastic neutron scattering (INS) to probe the phonon density of states (pDOS) for photoexcited tetracene and pentacene, in order to study the singlet fission mechanism in these materials. INS is a vibrational spectroscopy technique analogous to Raman spectroscopy. INS has several advantages over optical vibrational spectroscopy including no selection rules, measurement across a wider and lower energy range alongside momentum transfer, and very high sensitivity to hydrogen-rich materials, resulting in a spectrum that is a weighted density of phonon states.³⁰ Since protons generally terminate bonds on the borders of organic molecules, INS is particularly sensitive to intermolecular conformations. This makes INS particularly advantageous over optical vibrational spectroscopy techniques for studying organic materials.³¹ For the first time, we report in-situ excited state INS measurements on organic chromophores measured using a recently developed sample environment on the indirect geometry VISION neutron spectrometer at Oak Ridge National Laboratory.³² The sample environment uses continuous wave 405 nm (3.06 eV) and 520 nm (2.38 eV) lasers to photoexcite samples while simultaneously measuring INS in-situ. We measure the fractional differences between the optically excited and dark spectra and model the spectra using plane-wave density functional theory (DFT), showing that the measured spectral changes are due to excitons. The modeled excited state structures that are able to reproduce the INS spectra correctly are taken from the periodic DFT calculation and used

to calculate the electronic properties using time-dependent DFT (TD-DFT). The combined measurements and simulations demonstrate that the SF activation barrier is reduced in the excimer state by dynamic changes to the geometry of molecules surrounding the excimer itself.

Results and Discussion

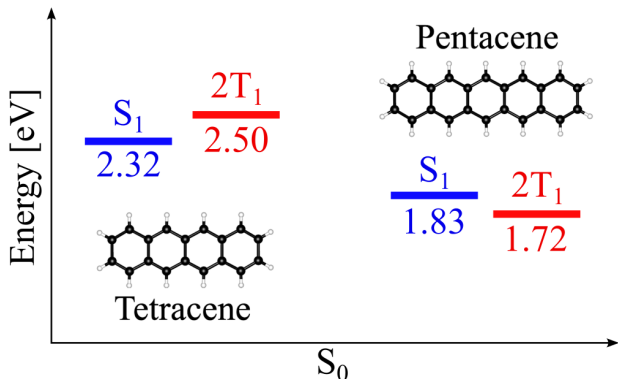


Figure 1: Electronic states diagram showing the ground state, first singlet and $2\times$ first triplet energy levels for tetracene (left) and pentacene (right).

Tetracene and pentacene are model molecules used in studying the SF mechanism,³³ containing four and five linearly fused benzene rings, respectively. Figure 1 shows the energy levels of the first excited singlet (S_1) and $2\times$ first excited triplet ($2T_1$), in blue and red, respectively, for tetracene and pentacene. $E(S_1)$ is 1.83 eV and $E(2T_1)$ is 1.72 eV for pentacene,^{34,35} resulting in a spontaneous unidirectional exoergic pathway for SF on the 80-100 fs timescale.³⁶⁻³⁹ On the other hand, tetracene has energy levels of 2.32 eV for $E(S_1)$ and 2.50 eV for $E(2T_1)$,⁴⁰ leaving a 0.18 eV energy barrier for SF to proceed. Despite tetracene's endoergic character, SF proceeds with very high quantum efficiency for both pentacene and tetracene.⁴¹

INS is measured for these model materials while photoexciting the samples in-situ using a recently developed laser-equipped optical excitation sample environment.³² Figure 2 shows the INS spectrum for crystalline pentacene with the lasers off and on. The blue line shows

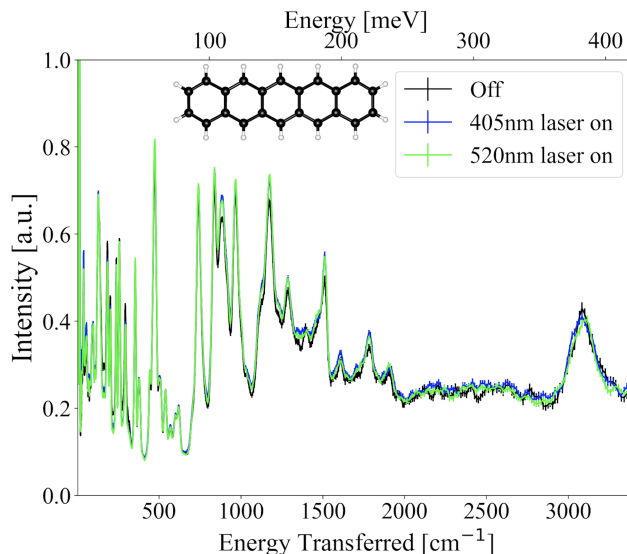


Figure 2: INS spectrum for pentacene with 405 nm laser on (blue), 520 nm laser on (green), and laser off (black).

the measurement with 405 nm laser on, green line shows 520 nm laser on, and black is for laser off. The S_n population has been shown to have a dependence on excitation energy by measuring stimulated emission in ultrafast measurements, finding that the excitation energies between 475-575 nm forms singlets,⁴² and is corroborated by photoluminescence studies.^{43,44} While pumping with 405 nm excitation energy was not performed, blue shifted pump sources (475 nm, 2.61 eV) have showed a population of 'hot' exciton states before relaxing to a short-lived S_1 .³³ Temperature dependent transient absorption measurements indicate SF is active down to 4 K.⁴⁵ INS measures the superposition of the pDOS of the sample, therefore a mixture of ground state and excited state molecules are present in the optically excited spectra. Very minor changes are seen between the laser off compared to laser on measurements, which is expected because only a fractional volume of the sample is in the excited state. The minor changes throughout the spectra are likely the result of slight changes in bond lengths and partial charge distributions after excitation including excimer states and locally distorted geometries of excited dimers.^{37,46} The acenes studied can also undergo [2+2] photodimerization⁴⁷ between neighboring molecules, but we have previously shown this solid-state reaction to be very slow in the cryogenic environment.⁴⁸

The INS spectral differences between the 405 nm and 520 nm lasers are mostly absent within the experimental error, indicating the lack of changes to the pDOS from optically excited states in pentacene. We can think of two possible reasons that this may be. 1. There may be a low population of exciton states due to less than ideal excitation wavelengths used in this study. INS may therefore not be sensitive enough to detect the excited species with the much higher proportion of ground state molecules. This highlights a limitation to the photoexcitation sample environment on the neutron spectrometer. Currently there is the new capability of optical excitation, but there is no possibility to simultaneously detect integrated transient absorption to verify the excited state populations. 2. It appears that pentacene undergoes smaller changes in excited state geometry and partial changes than tetracene in the excited state, so the spectral changes are more difficult to detect. The spectral differences between laser on and laser off are minor for pentacene, yet can be seen clearly in tetracene. While the two molecules only differ by one additional acene count, that alone may be influential enough on a four ring structure compared to five, as a larger aromatic structure could help stabilize structure changes and increase delocalization. With larger samples or more averaging, it could be possible to determine the excited state spectral differences with statistical significance.

The same measurement was performed for crystalline tetracene and can be seen in Figure 3. SF has been shown to occur for tetracene with various optical excitation energies and temperatures (2.43 eV, 2.58 eV, and 3.10 eV at 298 K, 77 K, and 4 K).^{28,33} The temperature independence was further supported by transient absorption measurements between 10-270 K in tetracene.²⁹ Like pentacene, tetracene shows similar minor changes to the INS spectrum when comparing laser off and on. For tetracene, the INS spectra of the samples excited with 405 nm and 520 nm lasers overlap within error throughout the spectral range, but deviate by more than the experimental uncertainty from the dark spectrum in several regions. Figure 3c shows the energy range \sim 100-150 meV, where most of the changes between the dark and photoexcited spectra occurs. This energy range, in general, corresponds to wagging, twist-

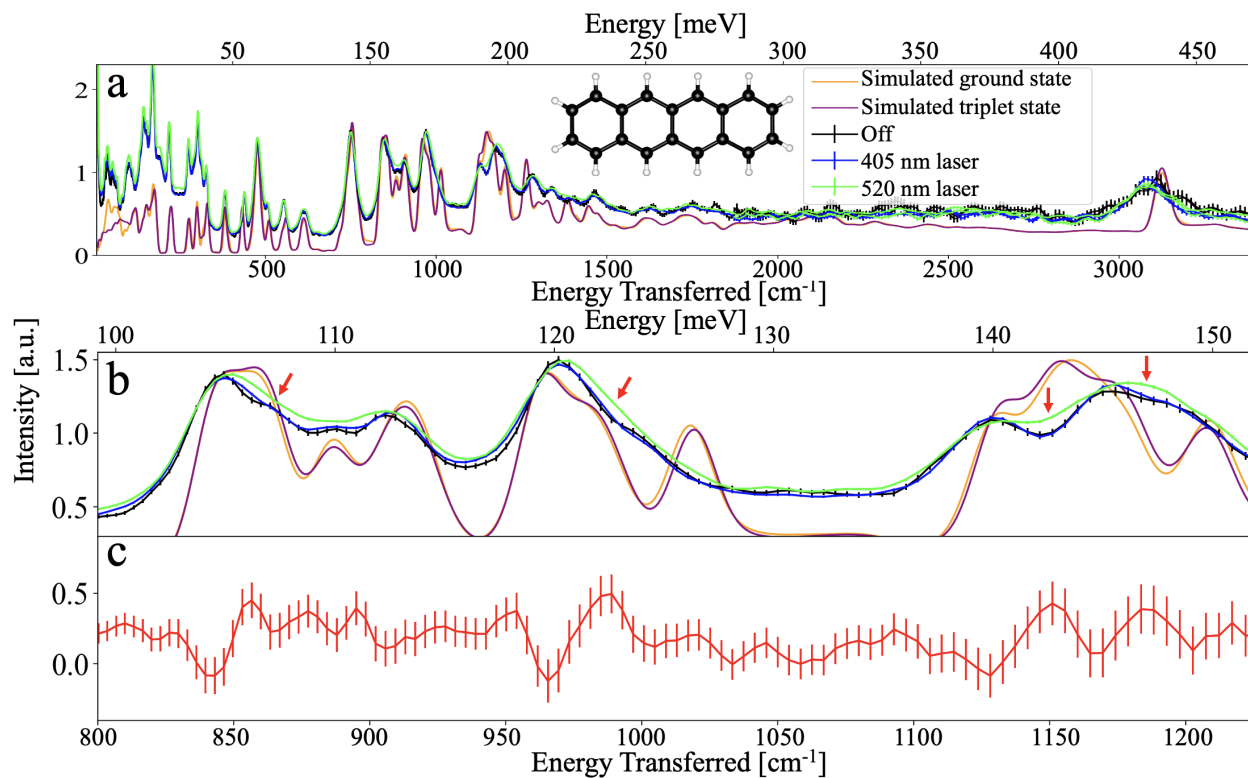


Figure 3: INS spectrum for tetracene with 405 nm laser on (blue), 520 nm laser on (green), laser off (black), and simulated spectra for ground (orange) and triplet (purple) states. Top shows INS of the entire energy range. Middle shows a close up of the spectra between ~ 100 - 150 meV. Red arrows highlight regions wherein spectral changes are observed for tetracene with and without photoexcitation laser use during INS measurement. Bottom panel shows the difference spectrum scaled by 4 between 520 nm laser on measurement and laser off.

ing, rocking, or bending motions for C—H bonds. Since INS spectra are heavily weighted by the contribution of protons, these modes provide detailed information about the external molecular environment and intermolecular packing. Both excitations produce an increase in phonon intensity for several peaks and some energy shifts with energies between ~ 100 - 150 meV. The spectral changes are due to the presence of long lived T_1 states. The lifetime of singlet states is far too short to be detectable. The spectral changes seen here are not consistent with dimerization of tetracene as demonstrated by our previous work on dimerization of optically excited anthracene.⁴⁸ A further confirmation that the spectral changes are due to the presence of T_1 states is that larger changes are seen for the 520 nm excitation. The absorption coefficient of tetracene is $>2\times$ higher at 520 nm than at 405 nm, while both laser power was measured to be 200 mW, so a larger excited state density with excitation at 520 nm is expected.⁴⁹

Previous 2D electron spectroscopy measurements show evidence of excitation energy dependent coherent vibrational modes coupling to overcome the SF energy deficit for tetracene.⁵⁰ This hypothesis posits that the 405 nm laser is able to excite higher energy singlet states ($S_{n>1}$) and fission to the $2T_1$ pair without the need for any vibronic coherence. This hypothesis was further corroborated by shaped pulse studies that show that the energy deficit for SF can be supplied optically with higher excitation energy.⁵¹ While the excitation energy of the 405 nm laser is able to excite $S_{n>1}$ above $2T_1$ and directly convert through SF, the 520 nm laser is only able to excite the S_1 states with excitation energy supplied by the laser below $2T_1$. Stern *et. al* posits that SF proceeds for a tetracene derivative by vibronic coupling to form $(TT)^1$, with $T_1 + T_1$ separation being thermally activated.⁵² However, the origin of the needed thermal energy for cryogenically cooled tetracene is unclear and so significant questions about the mechanism for SF remain.

The electronic structure for tetracene is first studied using TD-DFT. For a single gaseous tetracene molecule in the ground state, S_1 and $2T_1$ levels are calculated to be 2.29 eV and 2.42 eV, respectively, very close to the published experimentally measured values of 2.32 eV and

2.50 eV. In contrast to inorganic semiconductors that have rigid covalent bonds, molecular crystals are held together by weak Van der Waals forces that allow appreciable structural rearrangement of neighboring molecules during the electronic excitation due to changes in the local dipole moment. The combined deformations from the excited state molecule and the neighboring molecules can shift the electronic states with respect to the ground state geometry. To address the separate effects of excited state geometry and relaxation of the molecular lattice, we first optimized the geometry of a single gas state tetracene in the S_1 excited state using TD-DFT in Gaussian (details of this simulation in SI section 1.). Both the S_1 and T_1 energy levels were calculated with the S_1 excited state geometry. We found that the S_1 energy decreased to 1.97 eV, while $2T_1$ energy decreased to 1.59 eV. This reduction in the $2T_1$ energy with respect to the S_1 energy shows an avenue for SF that does not require additional energetic activation. This simulation addresses the change in excited state geometry for one molecule but ignores changes due to the local molecular environment of true periodic systems.

To account for the additional changes to the excited state geometry due to the molecular environment, the S_1 and $2T_1$ energy levels are further explored by using planewave DFT to include periodic effects. We have previously shown near quantitative agreement between experimental and simulated INS spectra across a wide energy range for molecular crystals. This close match between simulated and experimental INS data has enabled validation of the input structure and calculated phonons leading to accurate predictions of charge mobilities in molecular crystals^{53,54} and defect sites in metal organic frameworks.⁵⁵ The orange and purple spectra seen in Figure 3b,c show the simulated INS spectra for the ground and T_1 states of tetracene, respectively, from a molecular crystal consisting of an excited molecule surrounded by ground state molecules in a plane wave superlattice structure. Some of the predicted changes in the measured photoexcited INS spectrum are captured in the triplet INS simulation (details of the planewave simulations in Supporting Information section 1). At 107-108 meV, 121-124 meV and 144-148 meV the measured photoexcited spectra show

increased intensities and blue-shift that are captured in the simulated spectra. Also at ~ 143 meV the measured photoexcited spectrum shows increased absorbance that reduces the valley between peaks at 140 and 145 meV. The spectral changes are highlighted with the red arrows in Figure 3. The corresponding simulated spectra depict these increased intensities and the reduction of the valley is associated with a red-shift of the higher energy phonon. The phonon modes affected by the excited state geometry changes are depicted in Supporting information section S3. As seen in the supporting information figures, these phonons are associated with in- and out-of-plane motions of the protons of the tetracene and therefore are highly sensitive to the molecular environment and intermolecular packing of the molecules. In all, this shows that the plane-wave simulation is able to capture some of the phonon changes seen from the triplet induced deformations. As seen below, we will next use this geometric data to improve the TD-DFT simulations.

The unit cell of the tetracene crystal used in the ground state periodic plane wave simulations contain two molecules.⁵⁶ The local basis set TD-DFT is again used to re-calculate $E(S_1)$ and $E(2T_1)$ of the ground state molecules optimized with the planewave DFT geometry. The re-calculated $E(S_1)$ and $E(2T_1)$ are 2.24 eV and 2.31 eV for one molecule, and 2.23 eV and 2.29 eV for the other, respectively. This result shows a reduction in the activation energy needed for SF compared to the earlier ground state optimized geometry TD-DFT simulation. However, in general this simulation is less quantitative than the local basis set optimized geometry yet still predicts endoergic SF character. Next, the optimized excited state structure, used to model the excited state INS data, is taken from the planewave DFT and used to re-calculate $E(S_1)$ and $E(2T_1)$ using TD-DFT, resulting in 1.95 eV and 1.50 eV, respectively, for the photoexcited molecule, and 2.21 eV and 2.23 eV for the nearest neighbor. The excited state energy levels calculated are summarized in Figure 4. Typically this type of geometric simulation of excited states is not appropriate for simulation of excited state spectra because the electronic excitation is very fast compared to the relatively slower relaxation of nuclei towards its new relaxed excited state geometry. However, in this case the T_1 states

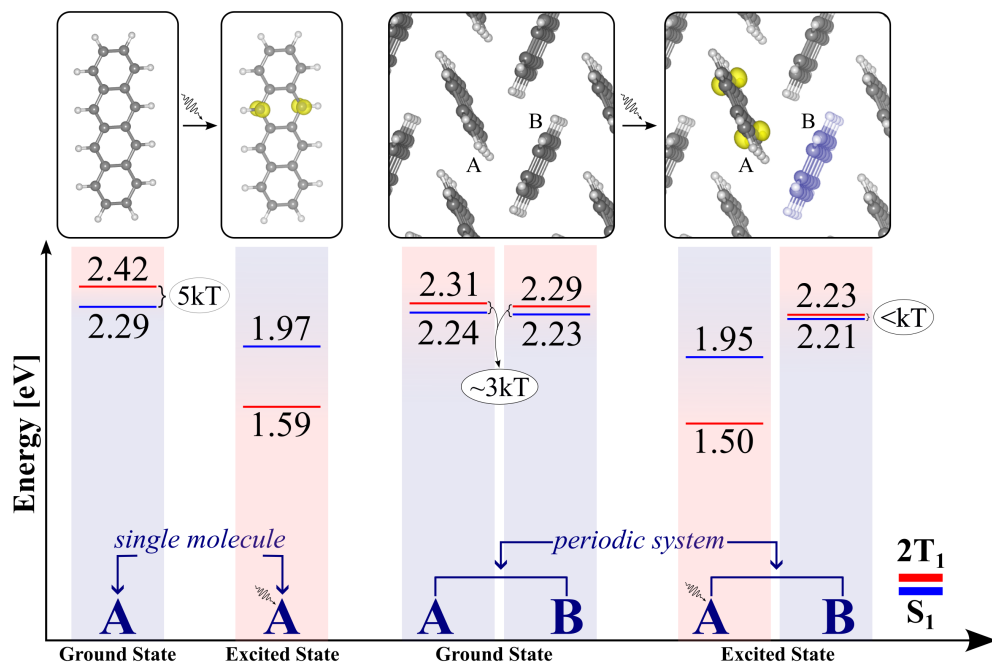


Figure 4: Energies for S_1 and $2T_1$ for tetracene calculated using local basis set TD-DFT. Single molecule calculation for the ground state molecule shows $E(S_1)$ and $E(2T_1)$ close to previously published experimental values. Excited state single molecule shows the energy levels calculated after relaxing the geometry in the S_1 state, wherein $E(2T_1)$ decreases by 0.70 eV leading to exoergic SF character. Periodic systems are the geometries taken from the ground state and triplet state INS model inputs. The periodic ground state $E(S_1)$ and $E(2T_1)$ for molecules A and B shows expected endoergic SF energy levels. The periodic excited state shows the same decrease in $E(S_1)$ and $E(2T_1)$ for molecule A as the single molecule calculation, and a decrease towards degenerate levels for molecule B.

captured in the cryogenic INS photoexcited spectra have lifetimes of seconds and so we can assume that the excited state geometry and surrounding molecules are fully relaxed. The formation of an excimer causes deformation of the neighboring molecules and the TD-DFT calculation shows that it can have a large impact on the electronic structure. While both excited state energy levels shift downwards in the excited state geometry, $E(2T_1)$ decreases much lower than $E(S_1)$ in one molecule. This result indicates that the favorable energetic level crossing for SF proceeds exoergically without the need for additional activation. This energetic shift may be due to the structural deformations to surrounding molecules which is caused by the dipole formation of the excited states.

The simulated $E(S_1)$ and $E(2T_1)$ for the excited state molecule using TD-DFT are very close to the calculated values of the local basis set optimized in the S_1 state, indicating that the energetics due to localization of an exciton and the resulting structural deformations are captured by the plane-wave DFT simulation. The neighboring molecule displays most of the energy shift that lowers the T_1 energy, resulting in $E(S_1) \sim E(2T_1)$. While these simulations show that the local electronic states in tetracene can shift due to molecular changes to enable SF without an energy barrier after the optical excitation takes place, it is unclear what occurs in the transition state. These measurements and simulations only capture the initial ground and final T_1 state geometries. It may be that a short lived S_1 state relaxes from the initial ground state geometry and via dynamic phonon motions the excited state relaxation $E(S_1)$ is just below $E(2T_1)$ resulting in SF to form the $(TT)^1$. Alternatively, nuclear relaxation reduces $E(S_1)$ with respect to $E(2T_1)$ but SF is still thermally activated. In this scenario, the local electronic states would allow both the thermal separation of $(TT)^1$, and the singlet regeneration from geminate triplets following SF from degenerate singlet and triplet pairs both previously observed in tetracene.^{29,52}

Conclusion

Inherently quantum mechanical processes, such as singlet fission, show promise to improve the efficiency of optoelectronic devices like photovoltaics, light emitting devices and photodetectors. This article demonstrates an expansion to the toolkit for studying dynamics and structure in excitonic materials. We show the use of an optically excited sample environment to measure optically excited vibrational spectra using inelastic neutron scattering for the first time. We used this new measurement technique to study the long lived triplet spectra of the small molecule organic semiconductors pentacene and tetracene. This pair of molecules is particularly interesting because both efficiently undergo singlet fission although the process is exoergic for pentacene but endoergic for tetracene. The excited state INS data provides information about the intermolecular environment around excited state molecules that cannot be measured with other vibrational spectroscopies. Detailed analysis using a combination of gas phase and plane-wave time dependent DFT shows that the molecular structure and partial charges on the excited molecule result in subtle shifts in the structure and partial charge distribution in neighboring molecules. These deformations result in local electronic shifts that dynamically lower the $E(2T_1)$ energy with respect to the $E(S_1)$ state in tetracene, perhaps revealing the reason that singlet fission in spite of an apparent energy barrier. This study highlights a new measurement technique and analysis that will be useful for the study of various other singlet fission and excitonic materials.

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Supporting Information Available

The supplemental information contains the methods for the INS measurement and INS spectrum for pentacene showing a narrowed energy range, the computational methods, and a study on the functionals for local basis set TD-DFT.

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TOC Graphic

